SUPPLEMENTARY MATERIAL

MATHCAD WORKING SHEET of a WORK

Analysis of enzyme-substrate interactions from square-wave protein-film voltammetry of complex electrochemical-catalytic mechanism associated with reversible regenerative reaction

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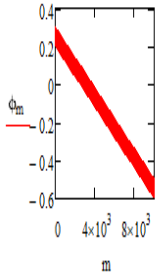
' Es := 0.25 ΔE := 0.004 Esw := 0.05

$m := 1..\frac{0.8}{\Delta E}\cdot 50$

$relativenpot_m := \left[\left(ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right)\cdot\Delta E + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - \Delta E\right]$ K := 10

$\phi_m := Es + Esw - relativenpot_m$



α := 0.5

F := 96500 n := 1 R := 8.314 T := 273.15 i := 1..1

$\gamma_i := 10^{-1.8+0\cdot i}$ $\lambda_i := 10$ n := 1

$k := 1..\frac{0.8}{\Delta E}\cdot 50$ $M_{k,i} := e^{-\frac{\gamma_i}{50}\cdot(k-1)} - e^{-\frac{\gamma_i}{50}\cdot(k)}$

$\log(\gamma_i) = \log(\lambda_i) =$

-1.8	1

$\gamma_i =$

0.0158

$\Phi_m := \frac{n\cdot F}{R\cdot T}\cdot\phi_m$

$$\Psi_{1,i} := \frac{\lambda_i\cdot e^{-\alpha\cdot\Phi_1}}{1+\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)\cdot\frac{M_{1,i}\cdot K}{\gamma_i\cdot(1+K)}+\lambda_i\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)\cdot\frac{M_{1,i}\cdot 1}{1\cdot(1+K)}}$$

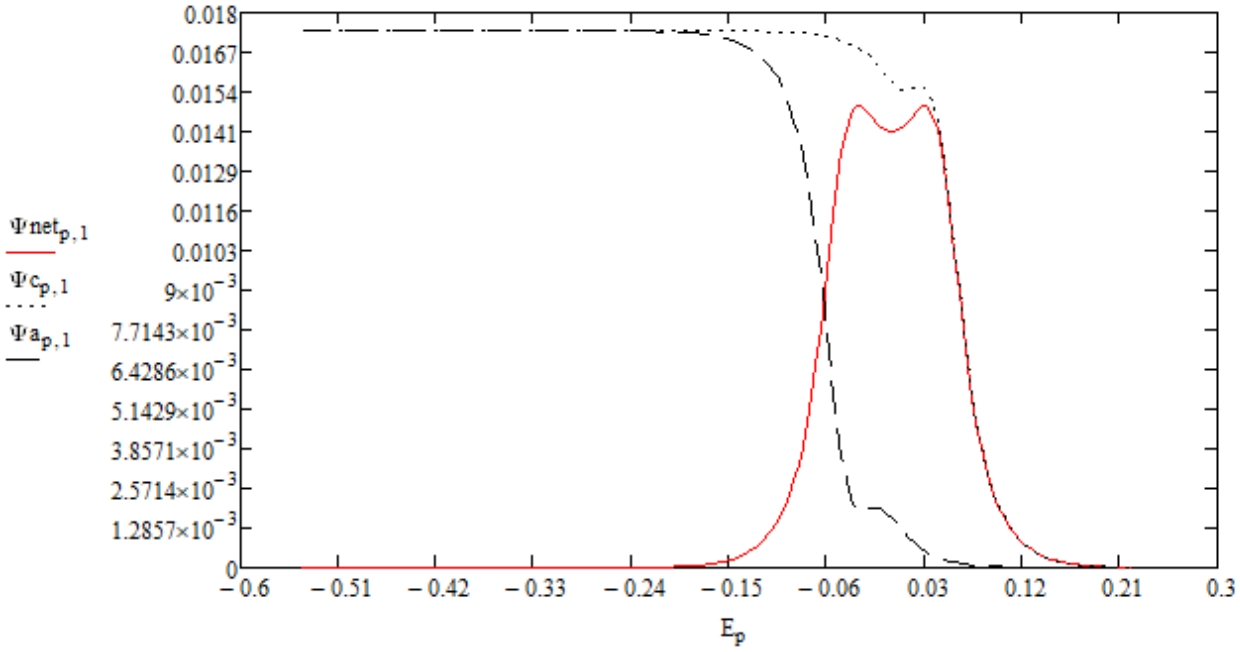
$$\Psi_{m,i} := \frac{\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left[1-\frac{\left(1+e^{\Phi_m}\right)\cdot K}{\gamma_i\cdot(1+K)}\cdot\sum_{j=1}^{m-1}\left[\Psi_{j,i}\cdot M_{(m-j)+1,i}\right]\right]-\frac{\left(1+e^{\Phi_m}\right)\cdot 1}{1\cdot(1+K)}\cdot\sum_{j=1}^{m-1}\left[\Psi_{j,i}\cdot M_{(m-j)+1,i}\right]}{1+\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot\frac{M_{1,i}\cdot K}{\gamma_i\cdot(1+K)}+\lambda_i\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot\frac{M_{1,i}\cdot 1}{1(1+K)}}$$

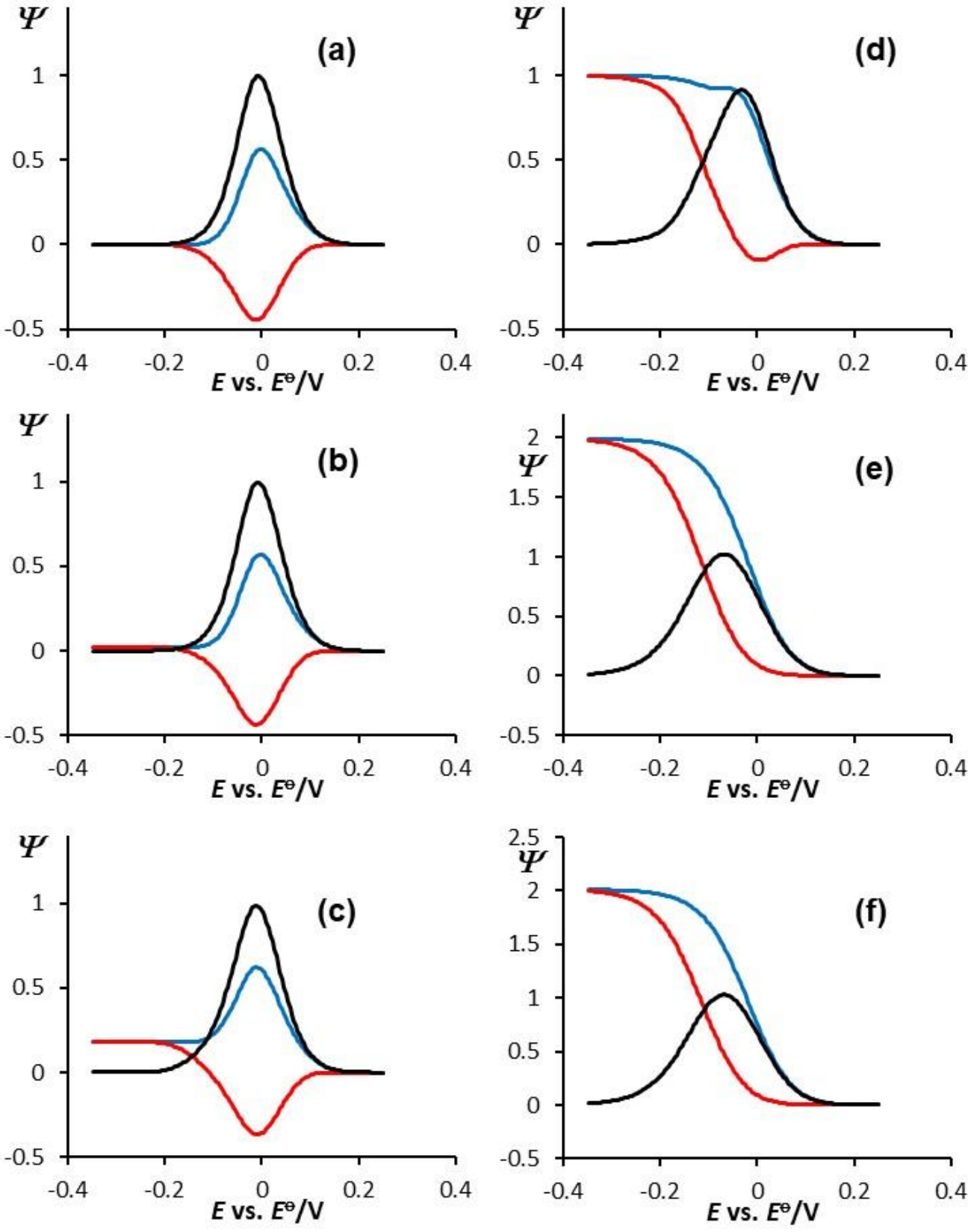
Surface catalytic EC' reversible mechanism

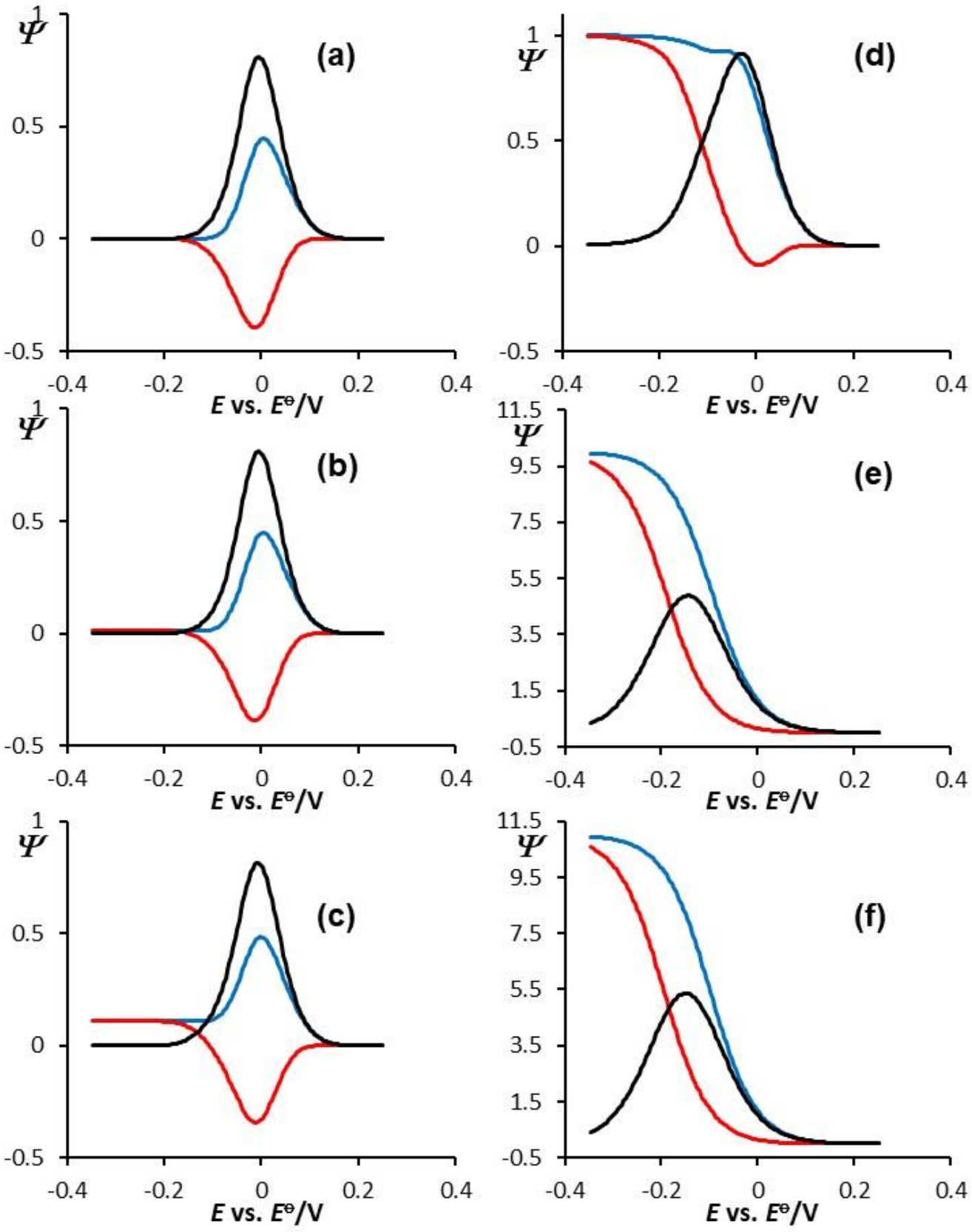
- **ΔE** is potential step
- **Esw** is square-wave amplitude
- **Es** is starting potential
- **m** is potential counter
- **φm** is dimensionless potential
- **F** is Faraday constant
- **R** is universal gas constant
- **T** is thermodynamic temperature
- **γ** is catalytic parameter
- **n** is number of exchanged electrons
- **λ = Ket -it** is dimensiolness parameter of electron transfer
- **α** is electron transfer coefficient
- **K =Keq-it** is equilibrium constant of regenerative chemical reaction
- **M** is numerical integration factor
- **Ψ** is dimensionless current

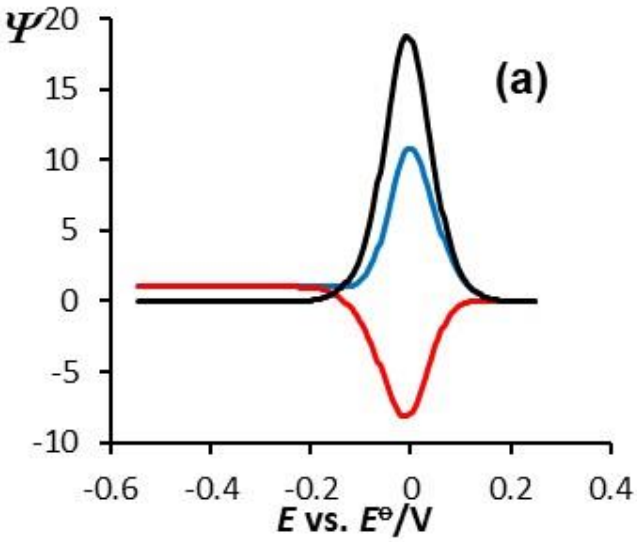
$$p := 0 .. \frac{0.8}{\Delta E} - 1 \qquad E_p := Es - p \cdot \Delta E$$

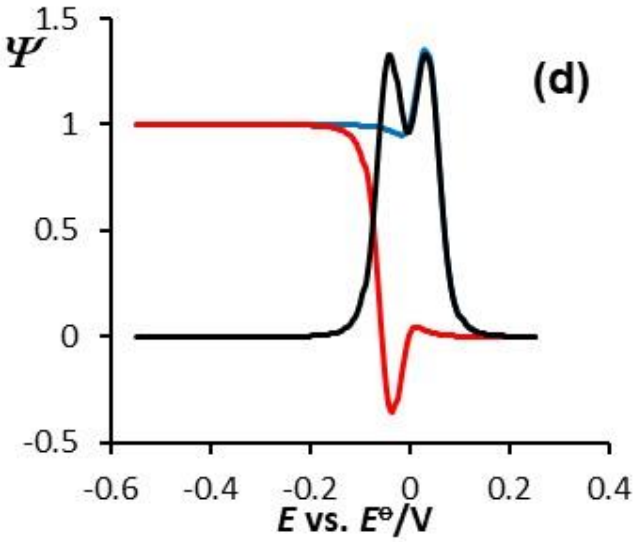
$$\Psi a_{p,i} := \Psi_{50 \cdot p + 25, i} \qquad \Psi c_{p,i} := \Psi_{(p+1) \cdot 50, i} \qquad \Psi net_{p,i} := \Psi c_{p,i} - \Psi a_{p,i}$$

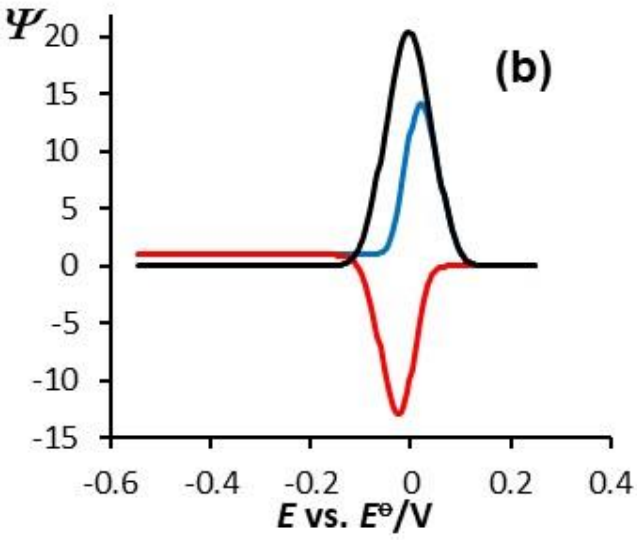


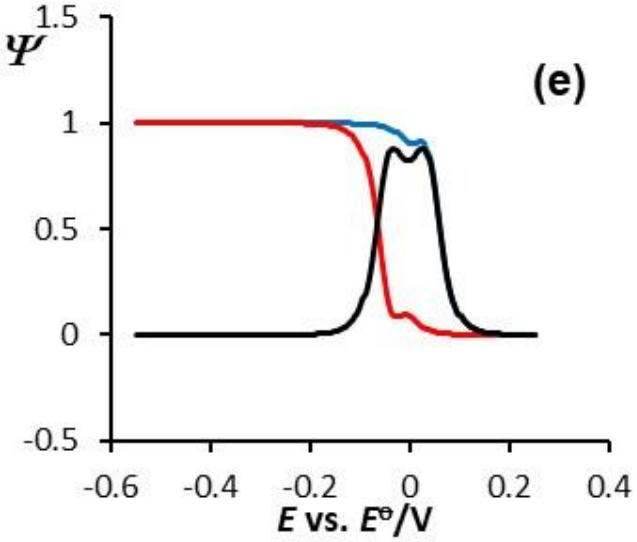

(a)
(b)
(c)
(d)
(e)
(f)
Ψ
E vs. E⁰/V

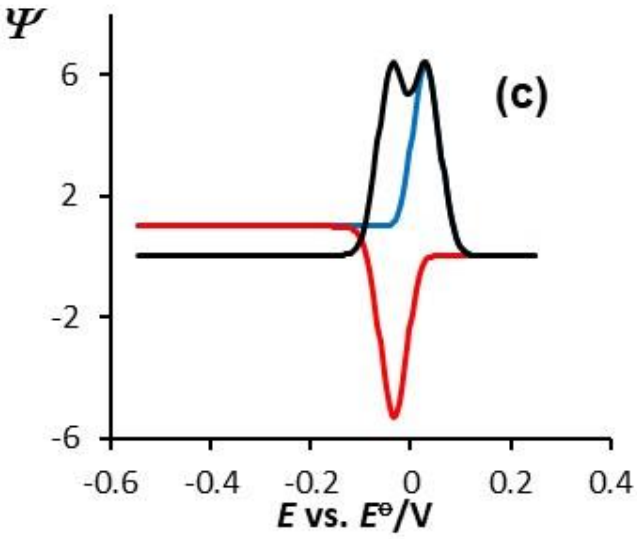

(a)
(b)
(c)
(d)
(e)
(f)
Ψ
E vs. E⁰/V
1
0.5
0
-0.5
-0.4
-0.2
0.2
0.4
11.5
9.5
7.5
5.5
3.5
1.5

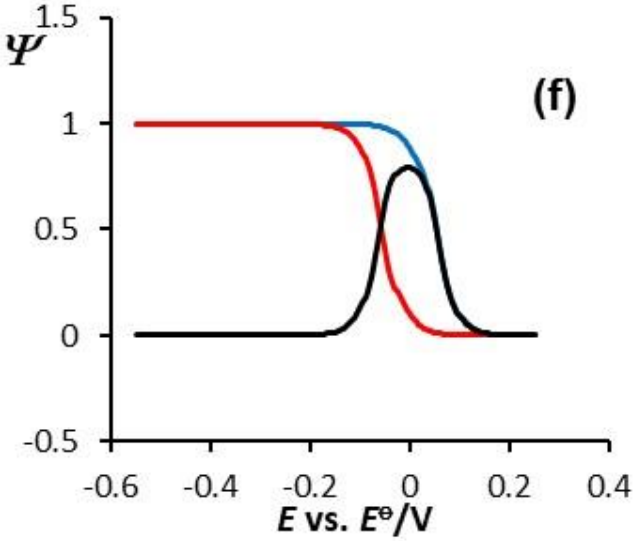

Ψ
20
15
10
5
0
-5
-10
(a)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V

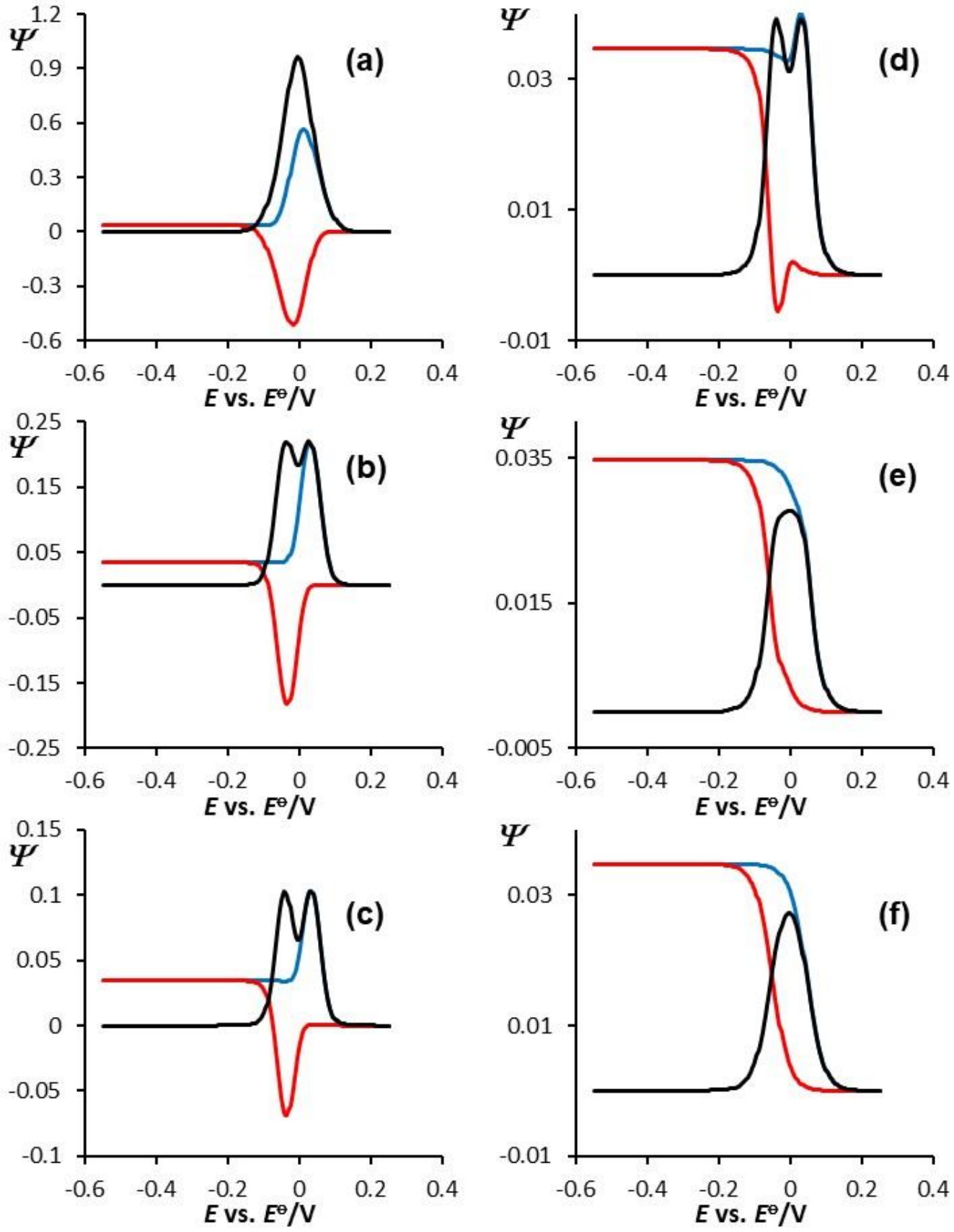

Ψ
1.5
1
0.5
0
-0.5
(d)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V

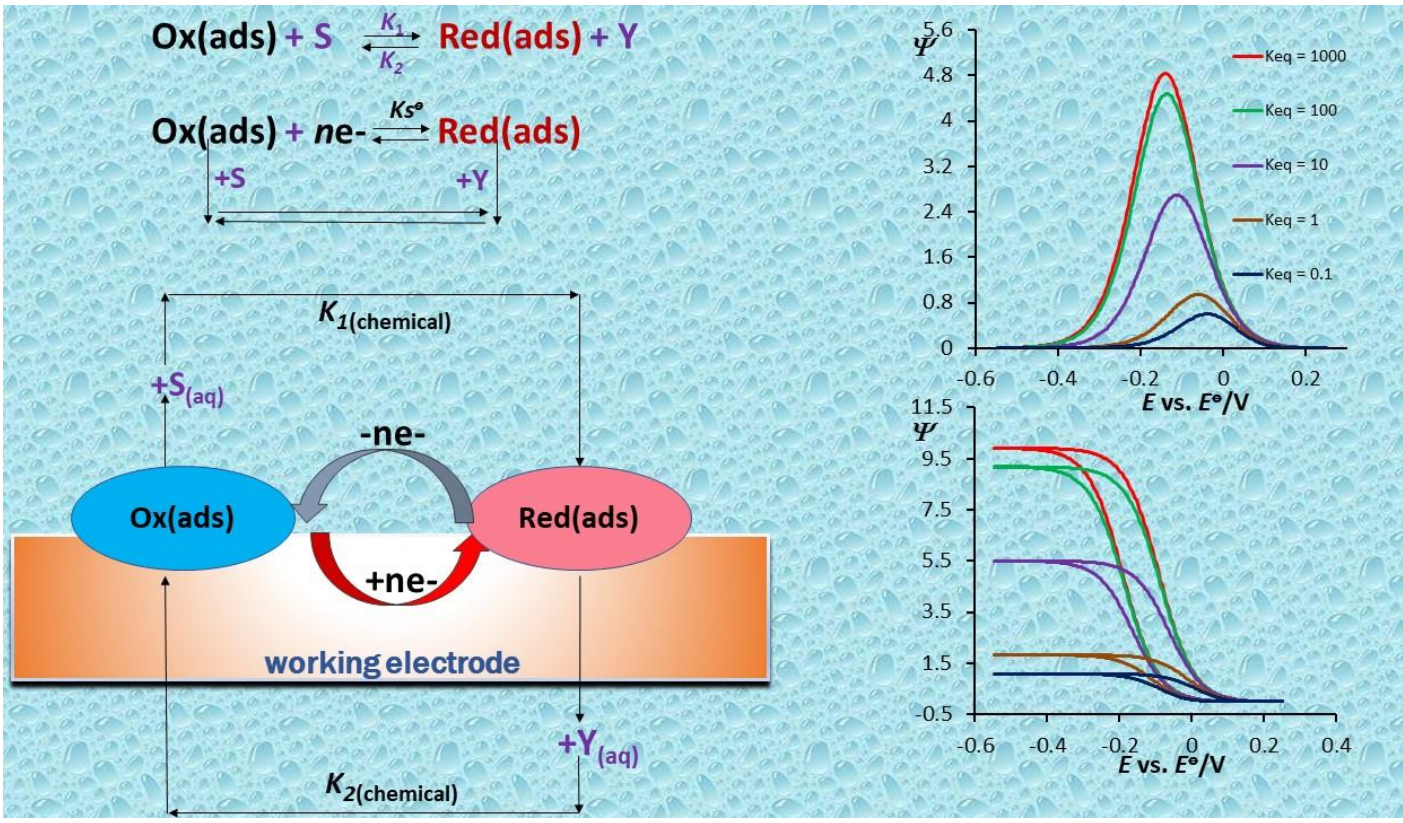

Ψ
20
15
10
5
0
-5
-10
-15
(b)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V


Ψ
1.5
1
0.5
0
-0.5
(e)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V


Ψ
6
2
-2
-6
(c)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V


Ψ
1.5
1
0.5
0
-0.5
(f)
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V


(a)
(b)
(c)
(d)
(e)
(f)
Ψ
E vs. E⁰/V
1.2
0.9
0.6
0.3
0
-0.3
-0.6
0.25
0.15
0.05
-0.05
-0.15
-0.25
0.1
-0.1
0.03
0.01
-0.01
0.035
0.015
-0.005
-0.6
-0.4
-0.2
0.2
0.4



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